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The Corrosion of Tin and its Alloys. Part I
The Tin-Rich Tin—Antimony—Copper Alloys

by

T. P. HOAR, M.A., Ph.D.

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THE CORROSION OF TIN AND ITS ALLOYS. PART I. THE TIN-RICH TIN—ANTIMONY—COPPER ALLOYS

BY

T. P. HOAR, M.A., Ph.D.

The International Tin Research and Development Council, composed of delegates appointed by the Governments of the principal tin producing countries, has been established for the purpose of acquiring and disseminating scientific and technical knowledge relating to tin, its alloys and chemical compounds, the processes involved in the production of these materials, and their applications.

The objects of the researches and other activities of the Council are to discover and develop new industrial applications of tin, to improve the existing products and processes, and to assist tin consumers in overcoming technical difficulties and problems relating to tin.

THE CORROSION OF TIN AND ITS ALLOYS. PART I.—THE TIN-RICH TIN–ANTIMONY–COPPER ALLOYS.*

By T. P. HOAR,† M.A., Ph.D., Member.

Synopsis.

The tin-rich tin–antimony–copper alloys have been examined with regard to their resistance to corrosion by dilute hydrochloric and citric acids and by various tap-waters. The straight 5 per cent. antimony alloy containing no copper is found to be usually somewhat more resistant to these types of corrosion than alloys containing copper.

Soft water produces tarnishing; hard water gives no tarnish, but may give localized attack if there is much chalky deposit.

I. Introduction.

Tin is well known as a metal distinctly resistant to many types of corroding conditions. It is used in the pure form as a protective coating for steel and for copper, and, alloyed with other metals, it forms useful corrosion-resistant materials such as the bronzes and pewters. In this series of papers it is proposed to make a preliminary survey of the nature and extent of the corrosion which occurs when tin-rich alloys are exposed to various dilute acids, salt solutions, and tap-waters.

The present report deals with the tin–antimony–copper alloys, which are extensively used as pewter. The behaviour of alloys of three different compositions has been examined and compared with that of pure tin.

Two methods of investigation have been used: (*a*) a series of measurements of the change of electrode potential with time of the alloys exposed to corroding media, which gives information as to the state of repair of the oxide-film on the metal surface and hence of the likelihood of corrosion occurring; ‡ and (*b*) qualitative and weight-change experiments with specimens partly immersed in various corrod-

* Manuscript received January 30, 1934. Presented at the Annual Autumn Meeting, Manchester, September 5, 1934.

† University Metallurgical Laboratories, Cambridge.

‡ May, *J. Inst. Metals*, 1928, **40**, 141; Hoar and Evans, *J. Iron Steel Inst.*, 1932, **126**, 379.

ing media, especially tap-waters, which is a state of affairs similar to practical conditions.

II. Materials.

Analyses of the alloys used are given in Table I. Micro-sections of certain cast and cold-rolled alloys are shown in Figs. 1–5 (Plate XII).

Table I.—*Analyses of Materials.*

Alloy.	Reference.	Tin, Per Cent.	Antimony, Per Cent.	Copper, Per Cent.	Lead, Per Cent.	Bismuth, Per Cent.	Iron, Per Cent.	Sulphur, Per Cent.
Chempur tin	TP	99·989	0·005	0·0004	0·002	0·0007	0·002	0·001
Tin	TC	99·679	0·225	nil	0·039	0·021	0·010	0·014
Pewter alloys	P 0	95·00	5·00	trace	nil	...	nil	...
	P 1	93·96	5·05	0·98	nil	...	0·01	...
	P 3	91·89	5·12	2·98	nil	...	0·01	...

All the materials were used in the cold-rolled condition. Specimens were cut 6·5 × 2·5 cm., and, except where otherwise stated, were abraded with Hubert IF emery, degreased with carbon tetrachloride, and stored in dry air over calcium chloride for 24 hrs. before the corrosion test.

III. Potential–Time Measurements.

The technique described in a previous paper was adopted,* so that a rapid survey of the electrochemical behaviour of the alloys could be made. As has been pointed out, a fall of potential with time indicates penetration and/or breakdown of the oxide-film by the electrolyte, which will usually cause corrosion, whilst a rise of potential with time indicates repair of the film and protection of the metal from corrosion. Of course, no indication of corrosion *velocity*, which may be very small even with a film-free metal, can be obtained by the method.

Some of the more significant of the potential–time curves obtained are shown in Figs. 6 and 7, each curve being the average of three concordant experimental curves.

Fig. 6 shows the behaviour of the alloys tested in the cold-rolled condition without abrasion with Cambridge tap-water as corroding medium (*vide infra*, Table II, for analysis). It will be seen that in all cases there is initially a very rapid fall of potential to about — 0·2 to — 0·3 v. on the normal hydrogen scale, indicating film-penetration by the electrolyte; this rapid fall is followed by a slow rise, doubtless because an insoluble corrosion product is being formed so close to the

* Hoar and Evans, *J. Iron Steel Inst.*, 1932, **126**, 379.

metal as to be precipitated in optical contact with it and so lead to film-repair. The general inference is that extensive corrosion is unlikely, and that any which does occur will be of a localized nature at especially weak places in the film which refuse to heal up.

Fig. 7 shows the behaviour of the alloys tested with 0·1*M* citric acid, used as being typical of the organic acids to which tin is exposed in canned fruits. In all cases there is a rapid fall of potential to about — 0·25 v. and no subsequent rise; this, in so acid a solution, undoubtedly indicates the probability of considerable corrosion.

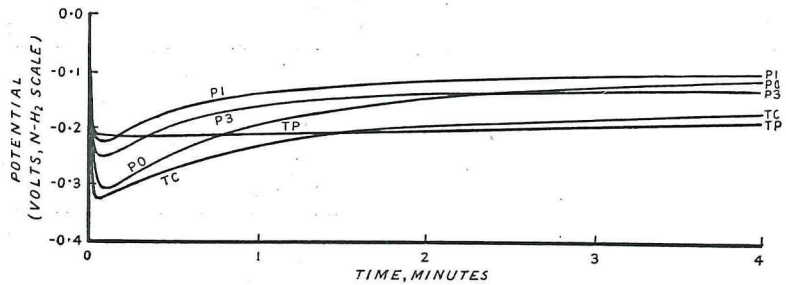

Fig. 6.—Potential–Time Curves in Cambridge Tap-Water.

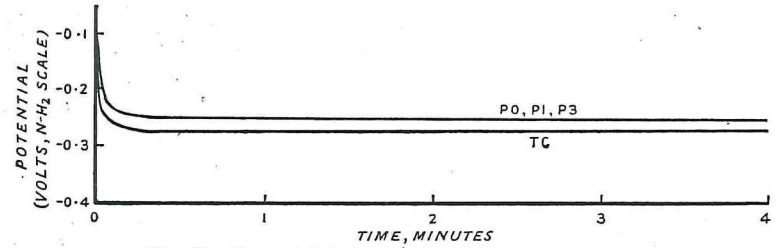

Fig. 7.—Potential–Time Curves in 0·1*M* Citric Acid.

It may be noted that there are no very significant differences between any of the potential–time curves of the alloys and the pure metal, except that P 0 shows a rise of potential rather more rapid than that of the other alloys. Much the same *probability* of corrosion may therefore be expected in all cases except that of P 0, which should be the least liable to attack. This conclusion has been borne out in further experiments which follow.

IV. Partly Immersed Corrosion Tests.

A series of weight-change corrosion experiments on materials TP, TC, P 0, P 1, and P 3 in 0·1*M* citric acid, 0·1*M* hydrochloric acid, and

Cambridge, London, and Birmingham tap-waters was carried out. The tap-waters were analyzed with the following results:

TABLE II.—*Analysis of Tap-Waters.*

	Cambridge.	London.	Birmingham.
	mg. equiv./litre.	mg. equiv./litre.	mg. equiv./litre.
Ca^{++}	4·65	1·54	0·41
Mg^{++}	0·08	0·12	nil
Fe^{+++}	nil	nil	nil
Na^{+} (difference)	0·40	0·76	0·15
	5·13	2·42	0·56
HCO_3^-	4·42	1·21	0·37
SO_4^{--}	0·32	0·59	trace
Cl^-	0·39	0·62	0·19
NO_3^-	trace	trace	nil
SiO_2	trace	trace	nil
	5·13	2·42	0·56
p_H of water	7·4	8·6	7·2

Weighed specimens 6·5 × 2·5 cm., prepared as described, were fixed vertically and symmetrically in uniform straight-sided beakers 8 cm. high × 4 cm. diameter, by means of a glass rod, a paper-clip, and soft wax, so that the immersed part of the specimen, 3·5 × 2·5 cm., was in contact with the solution only. The beakers were placed in large desiccator vessels of 5·5 litres capacity, which were arranged in an air thermostat * at 25° ± 0·05 C. The air in these vessels was swept out each day with fresh air in the acid runs where considerable corrosion occurred, but was unaltered in the tap-water runs where the total corrosion was very slight.

The acid runs were continued for 6 days, after which specimens were removed, washed, and dried. There was very little adherent corrosion product and the weight loss of the specimen may be taken as a measure of the corrosion (Table III). The tap-water runs were continued for some 50 days, when visible attack had occurred; it was not possible in the Cambridge and London water runs either completely to remove the corrosion product or to leave it entirely untouched, and the weight change is therefore little guide as to the amount of corrosion. However, the loss or gain in weight of these specimens with all *loose* corrosion product removed is included in Table III for completeness, and should be considered conjointly with the qualitative description of the corrosion which follows.

* Evans, *Chem. and Ind.*, 1931, **40**, 66, 245.

TABLE III.—*Weight Change of Tin and Pewter Specimens Partly Immersed in Corroding Media, 25·0° C.*

Solution.	0·1*M* Citric Acid. 6 days.	0·1*M* Hydrochloric Acid. 6 days.	Cambridge Tap-Water. 50 days.	London Tap-Water. 63 days.	Birmingham Tap-Water. 50 days.
Metal.	mg.	mg.	mg.	mg.	mg.
TP	−29·3	−36·1	−0·4	−0·1	+0·2
TC	−22·5	−32·7	−0·3	+0·1	+0·3
P 0	−25·5	−17·6	−0·3	±0·0	+0·3
P 1	−27·1	−17·5	−0·3	−0·1	+0·6
P 3	−28·3	−16·5	−0·4	−0·2	+0·6

Mean of duplicates.

The last three columns are semi-quantitative only, and must be considered with due regard to the qualitative description in the text.

Qualitatively, the corrosion showed many points of interest. It will be convenient to present the results for each corroding medium under separate headings.

(a) 0·1M *Citric Acid, 6 days.*—There was a very intense attack forming a rut parallel to and near to the water-line in every case,

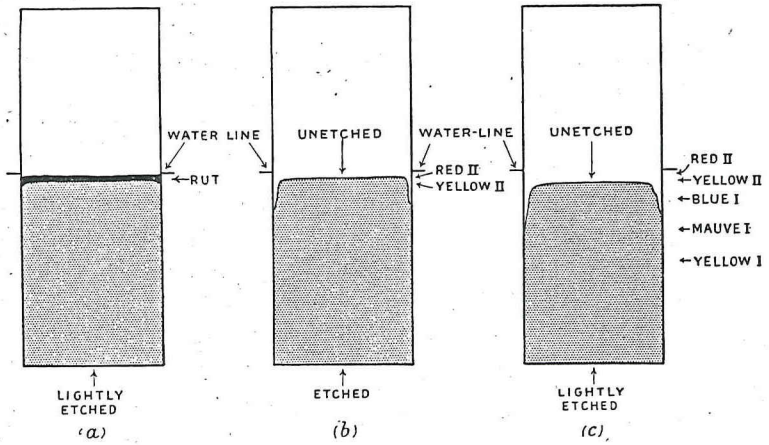

FIG. 8.—Distribution of Corrosion and Interference Tests.
(*a*) Tin and Pewter in 0·1*M* Citric Acid.
(*b*) Tin in 0·1*M* Hydrochloric Acid.
(*c*) Pewter in 0·1*M* Hydrochloric Acid.

although a very narrow strip in the "meniscus" appeared to be unattacked (Fig. 8 (*a*)). Lower down, there was much less attack, but the whole surface was lightly etched. A small amount of loose black deposit appeared at the water-line.

(b) 0·1M *Hydrochloric Acid*, 6 *days*.—The whole specimen was evenly etched, except for the part near the water-line, where interference tints indicating a film growing thicker towards the water-line were observed.* This is clearly a secondary film of tin oxides or hydroxides, and it is significant that it is thickest near the surface of the liquid where the oxygen supply is the most plentiful. The interference tints formed a band some 1–2 mm. wide in the case of the tin specimens TP and TC, but were spread out over some 15 mm. in all three specimens P 0, P 1, and P 3, containing 5 per cent. antimony, which it may be noted suffered much less corrosion (Table III). The distribution of the tints is shown schematically in Fig. 8 (*b*, *c*). The main part of the tinted area appeared to be lightly etched, indicating a very porous secondary film formed on it during attack; but the metal beneath the film in the band within 1–2 mm. of the water-line appeared quite bright and unetched, indicating that here the primary air-formed film never entirely breaks down.

(c) *Cambridge Tap-Water*, 50 *days*.—All the alloys except one P 0 specimen showed localized attack just below the water-line (Fig. 9, Plate XIII), and usually a number of minute "pin-holes" over the entire surface. Both forms of attack were most pronounced in the TC and P 3 specimens; TP and P 1 suffered less attack and P 0 scarcely any: there was a chalky deposit adhering to the specimen at the water-line.

(d) *London Tap-Water*, 63 *days*.—Local attack just *above* the water-line, where creepage of liquid had taken place, occurred most intensely on TC and P 3. There was less attack on P 1, scarcely any on TP, and none at all on P 0 (Fig. 10, Plate XIII). There was less chalky deposit than with Cambridge water.

(e) *Birmingham Tap-Water*, 50 *days*.—There was no localized attack on any specimen, but all were covered with a nearly uniform film showing interference colours varying between first-order yellow and first-order mauve. The increase in weight was small but measurable (Table III, col. 6), and indicates that the film produced on P 1 and P 3 was rather thicker than in the other cases.

Further qualitative partly immersed experiments were carried out in hot water, with (*a*) Cambridge tap-water, (*b*) Cambridge tap-water which had been previously boiled and the precipitate filtered off, (*c*) distilled water. Specimens were stood in beakers with 4 cm. immersed,

* It is well established that a thin transparent oxide-film on a metal surface yields an interference tint depending on its thickness and refractive index, in accordance with optical principles. With any one material, increase of thickness gives successively the colours yellow, mauve, and blue (first order colours), followed by a silvery region (the "hiatus") and then by yellow, red, and green (second order colours). After this the "overlapping" of the various orders produces results varying from one material to another.

and the beakers, covered with watch-glasses, were placed in a steam-oven which was run each day for 8 hrs. at about 95° C. for 20 days, being allowed to cool over-night. Evaporation was made good with distilled water each day.

The results with Cambridge tap-water were similar to those obtained in the cold, *viz.* local attack just below the water-line and "pin-holing," but, as expected, attack was considerably more rapid. In the boiled water, however, interference tints varying from first-order yellow to first-order mauve and blue, similar to those found with Birmingham water in the cold, were produced over the whole specimen, and very few points of local attack were noticed. Hot distilled water produced no local attack, but gave a similar although thinner film, which did not thicken above the first-order yellow in the case of TP and TC; such a film has also been observed on tin-plate exposed to hot distilled water for a few hours.* Except that all the pewters gave thicker films than TP and TC in the boiled and distilled water, no significant differences in the behaviour of all five materials were observed under hot-water conditions.

V. Discussion.

It will be seen from the foregoing results that the addition of 5 per cent. of antimony to tin (alloy P 0) is usually beneficial from the point of view of resistance to corrosion by the liquids used in this work. There is a slight reduction in the attack by citric acid in presence of air, and a marked reduction in the case of hydrochloric acid. The alloy containing 5 per cent. antimony was also much the least attacked of the series by cold Cambridge and London tap-waters.

The addition of 1–3 per cent. of copper to the 5 per cent. antimony alloy (P 1, P 3) proved detrimental in the conditions investigated. This is perhaps to be expected, since there is extremely little solid solubility of copper in the 95 per cent. tin–5 per cent. antimony alloy; † the copper phase can be seen in the photomicrograph of cast P 3 (2·98 per cent. Cu), Fig. 2, and being a "noble" heterogeneity, may well stimulate attack on the tin–antimony matrix under some conditions.

With regard to the mechanism of attack by the various media, only preliminary observations will be attempted here. It is well known that tin suffers practically no attack by cold dilute acids in the absence of air,‡ owing, no doubt, to its high hydrogen overpotential. The attack by 0·1*M* citric and hydrochloric acids in presence of air must therefore be associated with oxygen absorption.

* Macnaughtan, Clarke, and Prytherch, *Trans. Faraday Soc.*, 1932, **125**, 159.
† Tasaki, *Mem. Coll. Sci. Kyoto Imp. Univ.*, 1929, [A], **12**, 227.
‡ Mantell, *Amer. Inst. Min. Met. Eng. Tech. Publ.* No. **171**, 1929.

Some light is thrown on the corrosion mechanism in citric acid by the following measurements of electrode potential at various points on the corroding metal surface by the method previously developed during a study of the corrosion of iron.* In this technique, a capillary tube is arranged opening on to the metal surface at the point the electrode potential of which is required: through this capillary, liquid connection is made to a standard half-cell, and the e.m.f. of the cell

metal	corroding medium	standard half-cell

is then obtained on a valve electrometer. The potentials were measured against a quinhydrone half-cell made up in the same acid as the corroding medium: thus the potential against hydrogen in the same acid could be immediately found without any complication of liquid junction potential, and by a further measurement of the quinhydrone half-cell against a $N/10$ calomel half-cell through a saturated potassium chloride bridge, the potential of the corroding tin was obtained on the normal hydrogen scale. Readings were taken at several points near to the water-line and near to the lower edge of partly immersed specimens, at intervals for 48 hrs. Very concordant results were obtained, and average values are given in Table IV.

TABLE IV.—*Potentials Shown by Tin TC Corroding in Citric Acid Temperature* 18°–20° *C.*

Potentials in (*a*) volts against hydrogen in same acid are printed in italics.
(*b*) ,, ,, normal hydrogen electrode are printed in Roman.

Time, Hrs.	0·1*M* Citric Acid, p_H 2·14.				0·01*M* Citric Acid, p_H 2·78.			
	Water-line.		Lower edge.		Water-line.		Lower edge.	
1	*−0·172*	−0·296	*−0·182*	−0·306	*−0·126*	−0·287	*−0·133*	−0·294
2	*−0·168*	−0·292	*−0·176*	−0·300	*−0·127*	−0·288	*−0·136*	−0·297
24	*−0·165*	−0·289	*−0·172*	−0·296	*−0·129*	−0·290	*−0·138*	−0·299
48	*−0·157*	−0·281	*−0·163*	−0·287	*−0·126*	−0·287	*−0·135*	−0·296

Three points of major interest arise:

(1) The water-line potential is invariably some 5–10 mv. more noble than that at the lower edge. There must therefore be a small current of the differential aeration type flowing between the part of the specimen near the water-line and the part lower down. It is probable that most, if not all, of the mild corrosion of the lower part of the specimen can be accounted for in this way. It must, however, be remembered that citric

* Evans, Bannister, and Britton, *Proc. Roy. Soc.*, 1931, [A], **131**, 355; Evans and Hoar, *ibid.*, 1932, [A], **137**, 343.

acid causes a very intense corrosion at or near the water-line as well. It is not possible to measure the potential of the metal at the bottom of the "rut" formed by the water-line attack, so that information as to the possibility of a similar differential aeration mechanism applying here cannot be obtained.

(2) The potential of corroding tin in citric acid is considerably less noble than the hydrogen potential in the same acid. Were it not that tin has a particularly high hydrogen overpotential, hydrogen would be evolved; as it is, oxygen is necessary for the depolarization reaction and hence for corrosion.

(3) The potential of corroding tin, in both 0·1*M* and 0·01*M* citric acid, is about − 0·3 v. on the normal hydrogen scale, whereas the standard electrode potential of tin is given as − 0·136 v.* If therefore tin goes into solution as stannous ions according to the reaction $Sn \longrightarrow Sn^{++} + 2\varepsilon$ the concentration of Sn^{++} near to the metal surface must be very small, being on classical theory given by the equation:

$$-0{\cdot}3 + 0{\cdot}136 = \frac{RT}{2F} \log_e [Sn^{++}]$$

$$i.e.\ [Sn^{++}] = C\,.\,2 \times 10^{-6}\ N.$$

No doubt such calculations can give only qualitative results, but since after 48 hrs.' corrosion the total tin concentration in the solution is of the order of 3×10^{-3} *N*, there is a very significant discrepancy.

It is very probable that tin ions are removed by the citric acid with the formation of a citrato-complex. This hypothesis will be elaborated elsewhere; here it may be mentioned that an acid such as oxalic, which is known to form stable oxalato-complexes, corrodes tin much more rapidly and at a much lower potential than acids such as citric, and particularly sulphuric acid, where the complexes are considerably less stable. Riley † has recently directed attention to the effect of complex formation on the corrosion of copper and nickel by various acids, including citric acid; his conclusions have many points of similarity to the above views concerning tin.

It is proposed to make further potential experiments with hydrochloric acid. The formation of interference tints suggests that even in this strongly acid medium a certain amount of differential aeration occurs, under conditions of partial immersion.

The two quite different types of attack given by the tap-waters, *viz.* localized attack by the hard Cambridge and London waters, and film-thickening by the soft Birmingham water, are of great interest. Since

* Lewis and Randall, "Thermodynamics," p. 443. London: 1923.
† *Proc. Roy. Soc.*, 1934, [A], **143**, 399.

the film-thickening is also produced by hot distilled water, those waters in which the film does not thicken to interference-tint thickness must contain an inhibitor of the process. It seemed possible that this might be soluble calcium bicarbonate, when present in sufficient quantity, since hot Cambridge water from which bicarbonate and carbonate had been removed by boiling and filtering readily gave the thickening, whereas hot untreated Cambridge water did not. The latter must always contain an appreciable amount of soluble bicarbonate; under the alternate hot and cold conditions of the experiment it is to be expected that absorption of carbon dioxide from the atmosphere would occur during the cold period with consequent re-dissolution of some of the precipitated carbonate.

The hypothesis was verified by a series of 14-day tests with tin TC half-immersed in several mixtures of very dilute potassium chloride, to represent the "penetrating" type of ion present in tap-waters, and calcium bicarbonate, the supposed film-repairing agent. The results are summarized in Table V. It will be seen that increase of chloride concentration increases both the amount of film thickening and the tendency to break down at isolated points. Increase of calcium bicarbonate concentration decreases both the amount of film thickening and the local attack; at 0·005*N* the film remains below visible thickness, as in Cambridge tap-water containing about 0·0044*N*–HCO_3^- (Table II).

TABLE V.—*Effect of Calcium Bicarbonate on the Film-Thickening and Corrosion Produced by a Penetrating Anion (Cl^-).*

Conc. $Ca(HCO_3)_2$ → / Conc. KCl ↓	0	0·001*N*	0·005*N*
0	Film: yellow I — mauve I * Attack: none	Film: yellow I Attack: none	Film: invisible Attack: none
0·001*N*	Film: mauve I — blue I Attack: 1 local point, at water-line	Film: yellow I Attack: none	Film: invisible Attack: none
0·005*N*	Film: mauve I — 'Hiatus' Attack: 6 local points, all over surface.	Film: yellow I Attack: 3 local points, 1 at water-line.	Film: invisible Attack: 1 local point, at edge.

* See footnote to p. 140.

All specimens etched electrolytically.

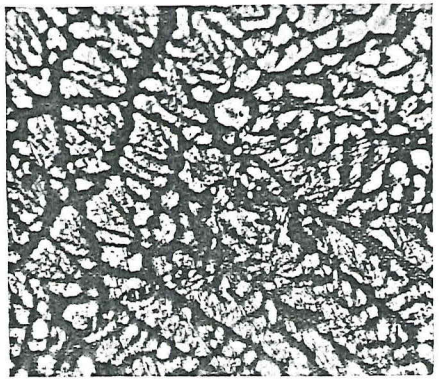

FIG. 1.—P 0. 95·00% Sn, 5·00% Sb. As cast. × 750.

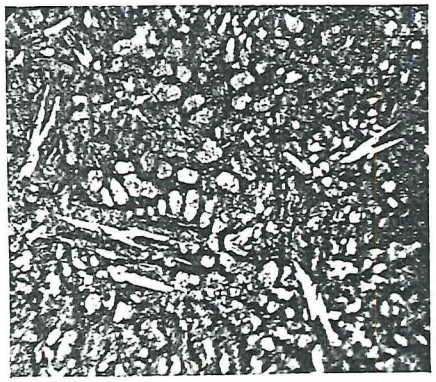

FIG. 2.—P 3. 91·89% Sn, 5·12% Sb, 2·98% Cu. As cast. × 750.

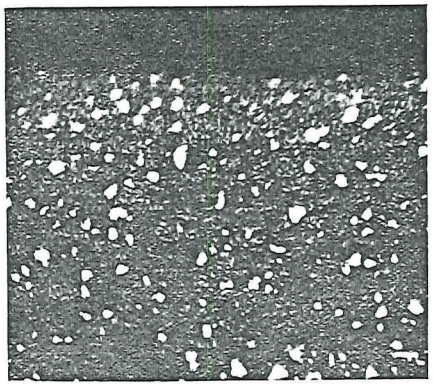

FIG. 3.—P 0. 95·00% Sn, 5·00% Sb. Cold-rolled; section. × 1000.

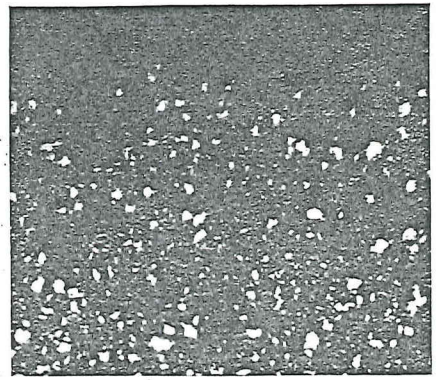

FIG. 4.—P 1. 93·96% Sn, 5·05% Sb, 0·98% Cu. Cold-rolled; section. × 1000.

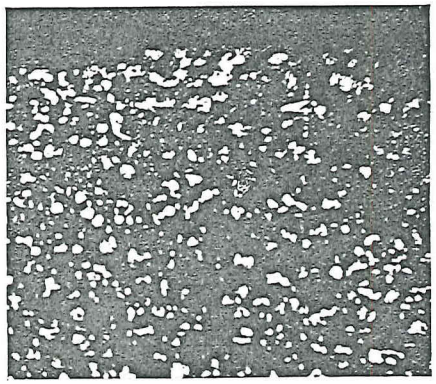

FIG. 5.—P 3. 91·89% Sn, 5·12% Sb, 2·98% Cu. Cold-rolled; section. × 1000.

[*To face p.* 144.

PLATE XIII.

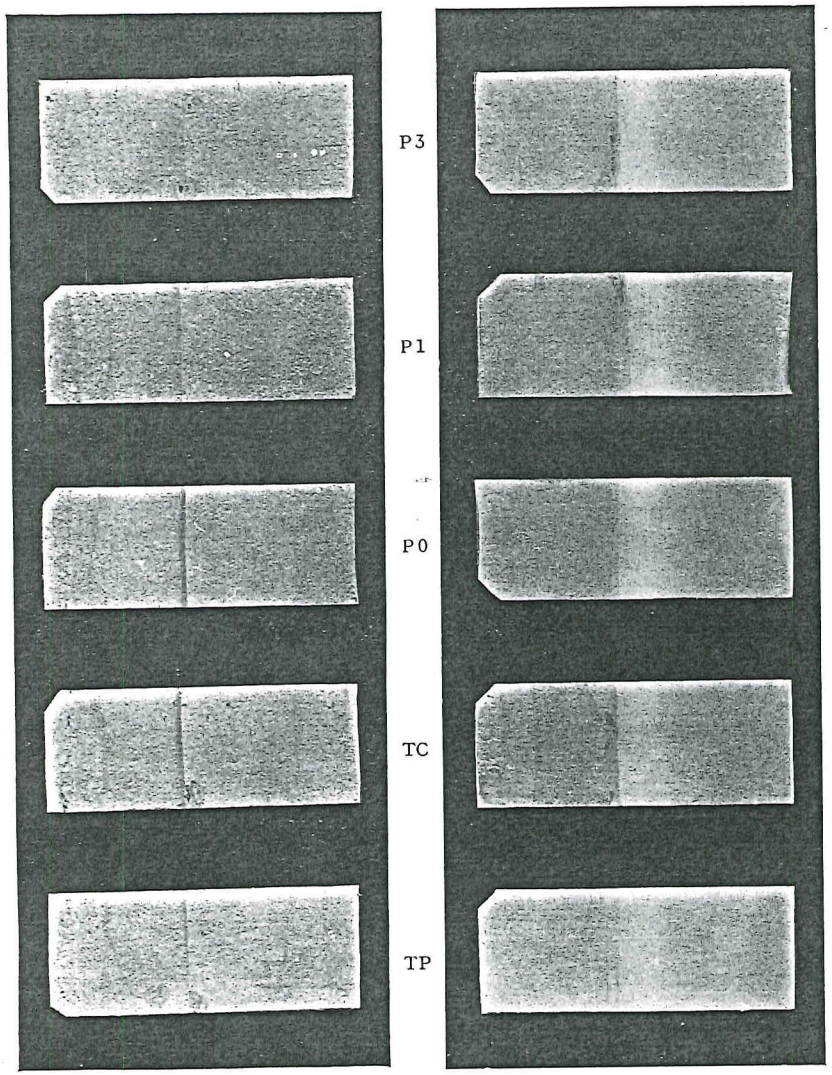

FIG. 9.—Corrosion in Cambridge Tap-Water.

FIG. 10.—Corrosion in London Tap-Water.

Precipitated carbonate is probably mainly responsible for the localized water-line attack found with hot and cold hard waters. Such attack did not occur except when precipitated carbonate was observed: thus a 14-day test of tin TC in Cambridge tap-water run concurrently with the tests of Table V gave only a minute trace of precipitate and no attack. The loosely adherent chalky deposit, found at the water-line of the specimen, might stimulate corrosion either by partly screening parts of the metal from oxygen access and so giving a differential aeration, or by assisting in the loosening of the otherwise protective film by surface tension effects. The "pin-hole" attack, found only in the very hard Cambridge water, may likewise be attributed to the precipitation of minute particles of carbonate all over the metal; the less hard London water gave much less precipitate and no pin-holing.

Finally, the creepage of the London water above the water-line is no doubt due to the high p_H, 8·6, of the water. The carbonate deposit, and the localized attack, was found in the creepage area.

VI. CONCLUSIONS.

This work indicates the desirability of incorporating about 5 per cent. antimony in tin from the corrosion-resisting standpoint, but suggests that the presence of 1–3 per cent. copper as well is deleterious

Tin and its alloys with small amounts of antimony and copper are corroded by dilute citric and hydrochloric acids in the presence of air. The addition of 5 per cent. antimony effects a marked reduction of the corrosion in hydrochloric acid, but is without much effect in citric acid.

Two kinds of attack are found in hot and cold tap-waters. In soft water, tin and pewter tarnish with the production of a visible film of interference-tint thickness. In hard water there is no tarnishing, owing to the film-repairing properties of calcium bicarbonate, but localized attack at the water-line and sometimes elsewhere occurs if a chalky deposit is formed from the water. Nevertheless, if care be taken to remove chalky deposits from a pewter vessel, there should be no attack in hard waters; fortunately such cleaning is likely to be the rule in good domestic practice. The straight 5 per cent. antimony alloy containing no copper proved to be, under the conditions studied, somewhat more resistant to tap-waters than alloys containing copper.

VII. ACKNOWLEDGMENTS.

The above work forms part of a programme being carried out by the International Tin Research and Development Council. My great thanks

are due to the Director of Research, Mr. D. J. Macnaughtan, for many stimulating discussions and for permission to publish.

I am grateful also to my colleagues, Mrs. F. D. Heywood, B.Sc., for carrying out the difficult and tedious photomicrographic work, and to Dr. W. D. Jones and Mr. W. E. Hoare, B.Sc., for the preparation of some of the rolled alloys.

University Metallurgical Laboratories, Cambridge.
March, 1934.

CORRESPONDENCE.

Mr. H. Stevens,* M.Sc. (Member): Comparatively little work has been published on the corrosion of tin and tin-rich alloys. Whilst much work has been carried out on corrosion in general, most attention has been directed to the more reactive metals, the so-called "noble" metals having been somewhat neglected. The present paper forms a welcome contribution to our knowledge of the latter, and it is to be hoped that the investigation will be considerably extended.

In the experimental work insufficient attention appears to have been paid to the preparation of the specimens. It is not clear whether all specimens were cold-rolled to the same extent; it is probable that differences in cold-rolling would leave the specimens in different conditions as regards internal stresses. Probably the pure tin, and some alloys, would recrystallize spontaneously at room temperature; but unless all the specimens had been stored at room temperature for considerable periods it does not follow that they would be free from internal stresses, and as these, if present, may affect the potential, it is better for them to be absent. The precaution of boiling the specimens in water for an hour or so would probably have removed internal stresses.

In the case of mild steel Homer † has shown that lines of abrasion may play a greater part in the progress of corrosion than inclusions in the metal; and, therefore, it is possible that in the case of corrosion of the alloys containing copper, the scratches caused by the emery paper may be as important controlling factors as the excess of the copper constituent.

In the preparation of tin alloys for microscopic examination it is very difficult to prevent the picking up of "dirt" from the emery paper, especially when the finest papers are not used, and, since the inclusions picked up from a Hubert IF emery would be fairly large, they may quite easily play a great part in the corrosion. This would apply particularly to the "pure" tin specimens, and the value of the results would thereby be somewhat diminished.

The preparation of specimens for work on corrosion is of great importance, and in the present paper there are at least three irregularities which may influence the results.

The Author (*in reply*): Each tin–antimony–copper alloy used in the work consisted of strip 0·050 in. thick which had been cold-rolled from ingots 0·3 in. thick; they are, therefore, strictly comparable with each other as regards mode of preparation. It is unlikely that the two varieties of "pure" tin, which were obtained as cold-rolled strip, contained any serious internal

* Metallurgist, Blakey's Boot Protectors, Ltd., Leeds.
† Homer, *Iron Steel Inst., Second Corrosion Report*, 1934.

stresses, and such stresses as may have remained in the harder cold-rolled alloys may be regarded as inherent qualities of such materials. The comparison of the corrosion of the five materials, therefore, seems to me to be a fair one.

Since all the materials were abraded under as nearly identical conditions as possible, it would appear that Mr. Stevens' second and third criticisms, regarding the possible effects of scratch lines and emery inclusions, are not valid; the alloys of different copper content *do* in fact behave differently, although identically prepared. If scratch lines and/or emery inclusions play important parts in determining the nature and extent of the corrosion, one would expect the differences due to the nature of the materials to be partially masked, and all the materials should suffer nearly similar attack. Yet the copper-bearing antimony alloys always give several well-defined points of attack in the hard tap-waters, whereas the straight antimony alloy containing no copper gives practically *none at all*. Clearly then the scratch lines and/or emery inclusions neither promote corrosion nor mask the effect due to the copper. In the case of the acid corrosion, the initial air-formed oxide film on the metal is very quickly dissolved, and the effect of possible breaks in it due to deep scratches or to emery inclusions cannot arise.

Mr. Stevens rightly emphasizes the importance of a proper preparation of corrosion specimens, a matter which has been repeatedly stressed by workers in this laboratory and others; but he is perhaps unfortunate in terming a uniform method of preparing specimens an "irregularity."

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